

**"Express Mail Post Office to Addressee" service Mailing Label Number
EV400233814US.**

PATENT
Atty Docket No.:
U 0132 OS/CRA

TITLE OF THE INVENTION

Coatings For Metal Containers, Metalworking Lubricant Compositions,
Compositions For Electroplating And Electrowinning,
Latex Compositions And Processes Therefor

5

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims priority, under 35 U.S.C. §119(e), of U.S. Provisional Patent Application Nos. 60/423,118, 60/424,249, 60/430,485, and 60/434,477, filed on November 1, 2002, November 6, 2002, December 3, 2002 and December 18, 2002, respectively, the entire contents of each of which are hereby 10 incorporated by reference.

BACKGROUND OF THE INVENTION

One of the last stages in the manufacture of aluminum cans and other metal containers such as ferrous metal containers is the application of one or more finishing coatings for decorative purposes and/or identification.

15

Such finishing coatings include acrylic paints, phenolic coatings which are used for baked can coatings, bitumen paints which are used for aluminum paints, coumarone-indene paints which are used to make aluminum paints, lacquers (which is a term also applied to the baking finish applied to the interior of food and beverage cans), and enamels.

Lubricating oils are fluids whose function is the reduction of friction and wear between solid surfaces, usually metals, in relative motion. Aside from the primary function of friction and wear control, lubricating oils are often called upon to serve other purposes, such as corrosion prevention, electrical insulation, power transmission, and cooling. The latter is particularly important in metal cutting and grinding.

There are two fundamental classes of lubricating agents, natural and synthetic. These lubricating agents include petroleum-derived oils, natural fatty acid esters, hydrocarbons prepared by the polymerization of olefinic hydrocarbons, polyalkylene glycol oils, synthetic esters which are primarily esters of dibasic acids or organic esters of phosphoric or silicic acid, silicone oils which are linear or cyclic siloxane polymers, halogenated hydrocarbons, perfluorinated polyalkylene glycols, polyphenyl esters, polyglycols, and neopentyl polyol esters.

In the production of metals by electrolysis of aqueous solutions, the electrowinning of the metals is usually carried out in tank cells. Developments in the electrowinning of metals from aqueous solutions have been directed toward improved anodes, improved additives, higher current densities, the use of ion-exchange membranes, better electrolyte quality control, and computer modeling of the processes.

Electroplating is the process of applying a metallic coating to an article by passing an electric current through an electrolyte in contact with the article. The ASTM adds some quality restriction by defining electroplating as electrodeposition of an adherent metallic coating on an electrode such that a surface having properties or dimensions different from those of the basic metal is formed.

Progress in electroplating is linked to improvements in materials of construction, power supplies and other plating equipment, purer industrial chemicals and anodes, improved additives for the plating baths, and improved analytical test and control methods. The quality of electroplating is dependent on the basic metal surface. Cleaner, less porous castings and better casing alloys, and improved steel and steel finishes have helped significantly.

Electroforming involves the electrodeposition upon a mandrel or mold in which the separated electrodeposit is the manufactured article.

The use of natural rubber in latex form for the preparation of rubber-containing articles is known.

5 However, the use of wetting and/or defoaming agents in natural rubber latex compositions has not been uniformly satisfactory, since a number of criteria must be met, e.g. the wetting and/or defoaming agent must not destabilize the latex composition, and the defoaming agent must be highly effective since otherwise small holes may be present in the finished article, which can be a serious
10 problem for dipped articles such as gloves for medical and surgical use.

BRIEF SUMMARY OF THE INVENTION

This invention relates to coatings for metal containers wherein the coatings contain at least one branched reaction product comprising the following reactants:

15 A) at least one compound of formula I



wherein each X group is a halogen atom or one X group is a halogen atom and two X groups represent an epoxy oxygen atom, which is attached to two adjacent carbon atoms in the R¹ group to form an epoxy group, and R¹ is an alkanetriyl group containing from 3 to 10 carbon atoms; and
20

B) at least one compound having the formula II



wherein R² is a substituted or unsubstituted, saturated or unsaturated, organic group having from 1 to 36 carbon atoms; X is -O-, -S-, or NR³- where R³ is hydrogen or a C₁-C₁₈ alkyl group; each AO group is independently an ethyleneoxy, 1,2-propyleneoxy, or 1,2-butyleneoxy group, n is a number of from 0 to 200, preferably from 1 to 100, more preferably from 2 to 20; and Y is hydrogen, or Y can be
25

a mercapto group or an amino group (amino or C₁-C₆ alkylamino group) in place of a terminal -OH group, provided that when Y is mercapto or an amino group, n is at least 1;

- wherein the mole ratio of the linking compound A) to B) is from 0.1:1 to 5:1,
5 preferably from 0.6:1 to 2:1 and more preferably from 0.8:1 to 1.5:1.

The presence of the above reaction product or products in the metal container coatings improves wetting of the substrate to be coated, improves the flow and leveling of the coating, improves the gloss of the dried coating, and enables the manipulation of the shear viscosity of spray applied coatings, i.e. the viscosity can
10 be either increased or decreased by selection of the molecular weight and quantity of the reaction product or products.

This invention also relates to lubricant compositions used for the working of metals. The term "metalworking lubricants" used herein is to be understood to include cutting fluids, boundary lubricants, and extreme pressure
15 lubricants.

The metalworking lubricant compositions of the invention comprise the following components:

- A) a lubricating oil; and
B) at least one branched reaction product comprising the following
20 reactants:

- a) at least one compound of formula I



wherein each X group is a halogen atom or one X group is a halogen atom and two X groups represent an epoxy oxygen atom, which is attached to two adjacent carbon atoms in the R¹ group to form an epoxy group, and R¹ is an alkanetriyl group containing from 3 to 10 carbon atoms; and
25

- b) at least one compound having the formula II



wherein R² is a substituted or unsubstituted, saturated or unsaturated, organic group having from 1 to 36 carbon atoms; X is -O-, -S-, or -NR³ where R³ is hydrogen or a C₁-C₁₈ alkyl group; each AO group is independently an ethyleneoxy, 1,2-propyleneoxy, or 1,2-butyleneoxy group, n is a number of from 0 to 200, preferably from 1 to 100, more preferably from 2 to 20; and Y is hydrogen, or Y can be a mercapto group or an amino group (amino or C₁-C₆ alkylamino group) in place of a terminal -OH group, provided that when Y is mercapto or an amino group, n is at least 1;

wherein the mole ratio of the linking compound a) to b) is from 0.1:1 to 5:1, preferably from 0.6:1 to 2:1, more preferably from 0.8:1 to 2:1, and most preferably from 0.8:1 to 1.5:1.

The presence of component B) in the metalworking lubricant compositions of the invention enhances the wettability of the lubricant and helps disperse metal fines. In addition, the lubricating and defoaming properties of the compositions are improved as well as their extreme pressure properties. The composition provides excellent wetting properties under dynamic and high shear applications without creating foam. Also, very consistent performance is obtained under a wide range of metal processing conditions.

This invention also relates to aqueous compositions for electroplating, electroforming, and/or electrowinning comprising:

- A) at least one metal or metalloid; and
- B) at least one branched reaction product comprising the following reactants:

- a) at least one compound of formula I



wherein each X group is a halogen atom or one X group is a halogen atom and two X groups represent an epoxy oxygen atom, which is attached to two adjacent carbon atoms in the

R¹ group to form an epoxy group, and R¹ is an alkanetriyl group containing from 3 to 10 carbon atoms; and

- b) at least one compound having the formula II



5

wherein R² is a substituted or unsubstituted, saturated or unsaturated, organic group having from 1 to 36 carbon atoms; X is -O-, -S-, or -NR³— where R³ is hydrogen or a C₁-C₁₈ alkyl group; each AO group is independently an ethyleneoxy, 1,2-propyleneoxy, or 1,2-butyleneoxy group, n is a number of from 0 to 200, preferably from 1 to 100, more preferably from 2 to 20; and Y is hydrogen, or Y can be a mercapto group or an amino group (amino or C₁-C₆ alkylamino group) in place of a terminal -OH group, provided that when Y is mercapto or an amino group, n is at least 1;

10

wherein the mole ratio of the linking compound a) to b) is from 0.1:1 to 5:1, preferably from 0.6:1 to 2:1, more preferably from 0.8:1 to 2:1 and most preferably from 0.8:1 to 1.5:1.

15

The presence of component B) in the aqueous compositions of the invention acts as an effective brightener in electroplating, electrowinning, and 20 electroforming baths. Component B) is a low foaming surfactant and is quite stable in both aqueous acidic and alkaline solutions. In addition, very consistent performance is achieved over a wide range of processing conditions due to the presence of component B) in the above aqueous compositions.

25

The present invention also relates to aqueous latex compositions which possess the above attributes, and which comprise the following components:

- I) a natural rubber; and

- II) at least one reaction product comprised of the following reactants:

- A) at least one compound of formula I



wherein each X group is a halogen atom or one X group is a halogen atom and two X groups represent an epoxy oxygen atom, which is attached to two adjacent carbon atoms in the R¹ group to form an epoxy group, and R¹ is an alkanetriyl group containing from 3 to 10 carbon atoms; and

- 5 B) at least one compound having the formula II



wherein R² is a substituted or unsubstituted, saturated or unsaturated, organic group having from 1 to 36 carbon atoms; X is -O-, -S-, or -NR³- where R³ is hydrogen or a C₁-C₁₈ alkyl group; each AO group is independently an ethyleneoxy, 1,2-propyleneoxy, or 1,2-butyleneoxy group, n is a number of from 0 to 200, preferably from 1 to 100, more preferably from 2 to 20; and Y is hydrogen, or Y can be a mercapto group or an amino group (amino or C₁-C₆ alkylamino group) in place of a terminal -OH group, provided that when Y is mercapto or an amino, or a C₁-C₆ alkylamino group, n is at least 1.

10

15

In the reaction products of component II), the mole ratio of the linking compound A) to B) is from 0.1:1 to 5:1, preferably from 0.6:1 to 2:1, more preferably from 0.8:1 to 2:1 and most preferably from 1.0:1 to 1.5:1.

20

Component II) is present in the aqueous natural rubber latex compositions of the invention in a wetting and/or defoaming effective quantity, which is usually in the range of from 0.001 to 5% by weight, preferably from 0.1 to 3% by weight, based on the weight of the aqueous latex composition.

25

This invention also relates to processes for preparing and methods for using the above latex compositions to form rubber-containing articles.

DETAILED DESCRIPTION OF THE INVENTION

Other than in the operating examples, or where otherwise indicated, all numbers expressing quantities of ingredients or reaction conditions used herein are to be understood as modified in all instances by the term "about".

5 Coatings for Metal Containers:

The metal container coatings of the invention contain from 0.001 to 5% by weight of the above branched reaction product or products, preferably from 0.1 to 3% by weight. These coatings normally contain at least one and usually a mixture of the following: binders, pigments, solvents, and additives.

10 Binders (or resins) are generally organic compounds, usually polymeric or oligomeric in nature, which provide a continuous matrix in the final film and have a major influence on the toughness, flexibility, gloss, chemical resistance and cure/dry properties of the coating.

15 Pigments are finely divided powders (particles between 0.1 and 50 micrometers in diameter) which are dispersed throughout the binder. In addition to reinforcing the final film, much as they do in composite plastics, they influence a coating's resistance to abrasion and are designed to react with the resin and become part of the binder system.

20 Major organic solvents include mineral spirits, ketones, acetates, alcohols, and xylene.

25 Among the more important classes of additives used in the coatings are: (a) surfactants, which are used to suspend pigment and binder particles; (b) thickeners to obtain proper rheology (especially in latex paints); (c) plasticizers, which lower the glass transition temperature of the binder and increase the flexibility of the coating; (d) antifoam agents to prevent bubbles in aqueous coatings; (e) antiskin agents, which prevent the formation of a dry layer on top of the coating while it is still in the container; (f) preservatives, such as biocides and mildewcides to protect the binder from microscopic organisms both before and after application; (g) ultraviolet light absorbers to protect the binder and/or substrate from degradation due to sunlight; and (h) a variety of surface conditioners and lubricants, which help

the film adhere to the substrate or protect the film by giving it a lubricated surface. Additives will often interact and coating formulators must be careful to watch for synergistic and antagonistic effects.

The branched reaction products used in the coatings of the invention
5 are low foaming surfactants, which can be used as the only surfactant in the coating compositions, or as a defoaming agent in conjunction with other surfactants.

The coating compositions of the invention can be used to coat metal cans and containers, especially aluminum cans used in the beverage and food industries, although other metal containers such as iron, steel, iron alloy, and the like
10 can also be coated with the coating compositions of the invention. Typically, primers or conversion coatings are applied first to the metal containers.

Where aluminum cans and containers are to be coated, conversion coatings such as amorphous phosphate coatings are generally applied first.

They provide a continuous uniform green coating with excellent
15 paint-bonding properties and underfilm corrosion protection. The coatings consist of varying ratios of chromic phosphate and hydrated aluminum oxide. The bath contains hydrofluoric acid, which removes the natural oxide to permit contact of the coating-forming chemicals with the metal. The complexity of the reactions involved makes it difficult to present a simplified chemistry, but the results of many tests and
20 analyses give the following coating composition: $x\text{CrPO}_4 \cdot y\text{Al}_2\text{O}_3 \cdot z\text{H}_2\text{O}$. The phosphate coatings vary from 10 to 300 milligrams per square foot (108 to 3228 milligrams per square meter), depending on the end use. The lower coating weights are used for paint bonding; the higher range is used for decorative purposes.

Gold-colored conversion coatings are formed in baths containing
25 hydrofluoric acid to remove the natural oxide, and chromic acid. The coating composition is chromic chromate plus varying amounts of hydrated aluminum oxide. Some baths also contain ferricyanide iron, which greatly accelerates the coating action and forms some chromic ferricyanide in the coating. This constitutes one of the most widely used conversion coatings on aluminum because of its high
30 speed, excellent corrosion resistance, and high affinity for organic finishes. The

hexavalent chromium content permits these coatings to withstand some what more severe corrosive environments than do the amorphous phosphate coatings. The baths have a pH of about 1.2 to 1.9 and can be applied by dip, brush, spray, or reverse roll coater.

5 Proprietary chromate rinses are frequently used over conversion coatings on aluminum for increased corrosion resistance.

Conversion coatings can also be applied by autodeposition.

Conversion coatings are of course undercoatings to which the finishing coatings of the invention can be applied.

10 The metal container coatings of the invention are nonaqueous compositions that include, but are not limited to, the following:

1. Enamels, which are types of oil-base paints containing binders that form a film by oxidation or polymerization on exposure to air and which have an outstanding ability to level off brush marks, etc., and form an especially smooth film. Enamels are usually intended for use as top coats and contain relatively less pigment than paint formulations for priming or surfacing. Enamels consist of an intimate dispersion of pigments in a varnish or resin vehicle. The vehicle may be an oil-resin mix or entirely synthetic resin. Those containing drying oils are converted to films by oxidation; those comprised wholly of synthetic resins may be converted by either heat or oxidation, or both.
2. Lacquers, which are protective or decorative coatings that dry primarily by evaporation of solvent, rather than by oxidation or polymerization. Lacquers were originally comprised of high-viscosity nitrocellulose, a plasticizer (dibutyl phthalate or brown castor oil), and a solvent. Later, low-viscosity nitrocellulose became available; this was frequently modified with resins such as ester gum or rosin. The solvents used are ethanol, toluene, xylene, and butyl acetate. Together with nitrocellulose, alkyd resins are used to improve durability. The nitrocellulose used for lacquers has a nitrogen content of 11-13.5% and is available in a wide

range of viscosities, compatibilities, and solvencies. Chief uses of
nitrocellulose-alkyd lacquers are for coatings for metal as well as other
products. Various types of modified cellulose are also used as lacquer
bases, combined with resins, and plasticizers. Many non-cellulosic
materials, such as dibutyl phthalate, butylbenzyl phthalate, vinyl and
acrylic resins are also used, as are bitumens, with or without drying oils,
resins, etc.

The term lacquer is also applied to the baking finish applied to the
interior of food and beverage cans.

- 5
 - 10
 - 15
 - 20
 - 25
 - 30
3. Baking finishes, which are paints or varnishes that require baking at temperatures greater than 66°C for the development of desired properties. Such finishes are based on oil-modified alkyd, melamine, epoxy, e.g. epoxy esters, nitrocellulose, or urea resins, or combinations of these. Baking is often done by infrared radiation producing high molecular weight coatings that are dense and tough.
 4. Other solvent-borne coatings containing resins such as alkyds (polyester resins made from polybasic acids and polyhydric alcohols), epoxides, polyurethanes, polyesters other than alkyds, and amino crosslinkers which are modified melamines.
 5. Thermosetting acrylic resin based coatings. The acrylic resins are monomer copolymers of acrylic acid or methacrylic acid esters. Some of the common monomers are methyl methacrylate, butyl methacrylate, methyl acrylate, butyl acrylate, ethyl acrylate, and 2-ethylhexyl acrylate. Thermosetting acrylic resins have at least one monomer belonging to the acrylic family which will react with itself or other resins at elevated temperatures to crosslink in order to cure. In addition to acrylic monomers previously mentioned, acrylonitrile, acrylamide, styrene, and vinyl toluene are often used in these polymers. Polymers which react to crosslink primarily because of hydroxyl groups are usually combined with an epoxy resin; those which react mainly with carboxyl groups

- usually are combined with an amine resin. Thermosetting acrylic paints are hard and stain-resistant and have high gloss.
6. Phenolic coatings, which contain phenolic resins as used in coatings are primarily made from phenol and para-substituted phenols reacted with formaldehyde to form methylol groups on the phenol ring. Condensation polymers are then produced by reacting these groups with phenol.
- 5 Phenolic coatings are fast drying and have high build and good resistance to moisture and chemicals. Phenolic coatings are sometimes used for baked can coatings, and oil-modified phenolaldehyde finishes are sometimes used for aluminum paints.
- 10 7. Polyurethane coatings are based upon reactions of isocyanates. Urethane coatings have excellent solvent and chemical resistance, abrasion resistance, hardness, flexibility, gloss, and electrical properties.
- The above coatings containing the above branched reaction product or products, can then be applied to one or more surfaces of metal containers.
- 15 Application methods include the use of air or airless spray equipment; electrostatic, hot or steam spraying; and the use of dip, or flow coating. With electrostatic spraying, the atomized coating is attracted to the conductive object to be coated by an electrostatic potential between the
- 20 coating and the object. Very little coating is lost with this process, and irregular objects can be coated uniformly. Heat spray application consists of heating the coating so that it is more fluid and higher-solids coatings can be applied. With steam spraying, steam is used to atomize the coating. Two-component spray equipment consists of two material lines to the spray gun so that two materials, e.g., an epoxy and a catalyst,
- 25 can be mixed in the gun just before application.

In the branched reaction products used in the metal container coating compositions of the invention, the linking compound of formula I in component A is preferably epichlorohydrin or another epihalohydrin. However, trihaloalkanes can be used, such as 1,2,3-trichloropropane, 1,2,4-trichlorobutane, 1,3,6-trichlorohexane,

and the like. Instead of chlorine in the epihalohydrins and trihaloalkanes, the corresponding bromine and iodine compounds can also be used, including compounds containing two or even all three of the above halogens.

The component B) compounds of formula II are organic (optionally 5 alkoxylated) alcohols or the corresponding sulfhydryl or amine compounds.

The R² group can be a substituted or unsubstituted, saturated or unsaturated hydrocarbon group having from 1 to 36 carbon atoms. Examples of such hydrocarbon groups include linear or branched alkyl groups having from 1 to 10 36 carbon atoms, preferably from 4 to 22 carbon atoms, linear or branched alkenyl or alkynyl groups having from 2 to 36 carbon atoms, preferably from 4 to 22 carbon atoms, aryl groups having from 6 to 22 carbon atoms, and arenyl groups having from 7 to 36 carbon atoms. Arenyl groups are alkyl-substituted aromatic radicals having a free valence at an alkyl carbon atom such as a benzylic group.

The R² group can also be a saturated carbocyclic group, an 15 unsaturated carbocyclic group having one or more multiple bonds, a saturated heterocyclic group, an unsaturated heterocyclic group having one or more multiple bonds. Any of the above R² groups can be substituted groups, i.e. the groups can be single or multiple substituents such as a sulfur functionality such as a mercaptan or thio group; a nitrogen functionality such as an amine or amide functionality; an 20 alcohol functionality, a silicon functionality, e.g., a siloxane; an ether functionality, e.g. a C₁-C₆ alkoxy group, or any combination thereof.

The R² group in formula II is preferably a branched chain alkyl group containing from 4 to 36 carbon atoms, preferably from 4 to 12 carbon atoms, and more preferably from 8 to 12 carbon atoms.

When the X group of formula II is an -S- group, the R² group will 25 preferably have from about 4 to about 22 carbon atoms, examples of which include but are not limited to, dodecyl mercapto and 1-hexadecanethio.

When the R²X-group of formula II is a secondary or tertiary amino group, the group preferably contains from 4 to 22 carbon atoms, and n is preferably 30 a number of from 1 to 50. Examples of primary and secondary amines useful for

obtaining the R^2X -group include, but are not limited to, cyclohexyl amine, isodecyl amine, and dioctylamine.

- 5 Optionally an additional component C) can be reacted with the linking agent of formula I and the compound of formula II. A glycidyl ether or amine can be added to the reaction of formula I and formula II. The amount of the glycidyl ether or glycidyl amine is from about 1 to about 20 mole percent based on the moles of the compounds of formula II used in the reaction. When the glycidyl ether or glycidyl amine is added, the ratio of component A) plus the glycidyl ether or glycidyl amine to component B) is preferably from about 1.2:1 to about 5:1.
- 10 Examples of glycidyl ether include, but are not limited to, PEG 600 diglycidyl ether, TETRONICTM 701 tetraglycidyl ether, triglycidyl di or triethanolamine, polyoxyethylene (POE) 200 tallow amine diglycidyl ether, propoxylated (POP10) trimethylol propane triglycidyl ether, propoxylated (POP7) pentaerythritol tetraglycidyl ether. Examples of glycidyl amines include, but are not limited to, tetraglycidyl 1,6-hexane diamine, tetraglycidyl JEFFAMINETM EDR-148, and tetraglycidyl isophorone diamine.
- 15

When Y in formula II is an amine or sulphydryl group, the resulting compounds can be readily prepared from the corresponding alcohols wherein the terminal hydroxy group is replaced by an -SH group or by an amine nitrogen. For 20 example, a compound of formula II where Y is -OH can be subjected to a catalyzed ammoniation (with ammonia, or a lower alkylamine) for replacement of the hydroxyl, or to a capping of the hydroxyl with epichlorohydrin followed by ammoniation (with ammonia, or a lower alkylamine) of the resulting glycidyl group.

In the compounds of formula II, the AO groups when present are 25 preferably all ethyleneoxy groups. However, as stated above, each OA group can be independently an ethyleneoxy (EO), 1,2-propyleneoxy (PO), 1,2-butyleneoxy (BO) group, i.e. any one or more of such groups can be present, and they can be present in any order, as well as be present in blocks, e.g. compounds of formula III:



wherein R² has the meaning given above, m is a number of from 0 to 100, preferably from 1 to 50, p is a number of from 0 to 50, e.g. from 1 to 50, and q is a number of from 0 to 50, e.g. from 1 to 50. Compounds of formula III in which R² is a branched chain alkyl group having from 4 to 12 carbon atoms, m is a number of from 2 to 20, and p and q are 0 are preferred.

The degree of hydrophilic and hydrophobic properties of the reaction products of components A) and B) can be readily controlled by controlling the type and number of alkyleneoxy groups in component B). For example, the greater the number of ethyleneoxy groups present, the greater the water solubility, while the presence of 1,2-propyleneoxy groups and/or 1,2-butyleneoxy groups for example, will decrease water solubility.

In general, the compounds of formula III wherein the sum of n, m, and p is at least 1, and especially at least 2 are preferred for use herein.

The branched reaction products used in the practice of the invention can be prepared by reacting components A) and B) (and C if present) together, preferably in the presence of an inert organic solvent, preferably a solvent such as toluene that will azeotrop with water, and in the presence of an inorganic base such as an alkali metal hydroxide, e.g. aqueous sodium hydroxide or potassium hydroxide, at a temperature in the range of from 60 to 125°C. In a preferred embodiment of the process, component B) is first mixed with the base, and the organic solvent, if present, and water is removed, e.g. by azeotropic distillation. Then component A) (and C, if present) is slowly added and the reaction continued until the reaction is completed. The reaction mixture is filtered and the filtrate vacuum stripped to remove any organic solvent.

Inert organic solvents that can be used in the above process are nonmiscible with water and nonhydroxylic. Examples of such solvents include toluene, CHCl₃, CH₂Cl₂, chlorobenzene, acetonitrile, and petroleum ethers, preferably toluene.

This invention will be illustrated but not limited by the following examples.

EXAMPLES

Example 1

Preparation of the reaction product of decyl alcohol · 4EO and epichlorohydrin

About 150 grams of decyl alcohol ethoxylated with an average of 4 moles of ethylene oxide (0.45 OH equivalents) were mixed with 385 grams of toluene and 54 grams of 50% aq. NaOH (0.675 equivalents). The water was removed by azeotropic distillation and when a moisture level of less than 0.8% was reached, about 46 grams (0.51 equivalents) of epichlorohydrin were slowly added. This mixture was allowed to react at 100° to 110°C for 24 hours. An aliquot of this mixture was removed and filtered to remove the NaCl and vacuum stripped to remove the toluene to give an amber, easily pourable liquid product that was dispersible in water.

Example 2

To an Acryloid™ Coating Resin (acrylic ester polymers in an organic solvent solution) is added 1.0% by weight of the reaction product of Example 1.

Two piece clean aluminum cans are coated with the above mixture by dipping the cans into a vat containing the mixture.

The cans are dried, leaving a clear resistant coating on the metal surfaces of the cans. The coating has high gloss and is highly uniform, without discernable bubbles or pits.

Example 3

Preparation of the reaction product of octyl alcohol · 4EO and epichlorohydrin

About 200.0 gm (0.654 hydroxyl equivs.) of octyl alcohol ethoxylated with an average of 4 moles of ethylene oxide was mixed with 400 gm toluene and 78.4 gm (0.98 equivs.) of 50% NaOH. Water was removed by azeotropic distillation until the level was below 0.8%. The mixture was cooled to 80°C. and 67.2 gm (0.72 moles) of epichlorohydrin was added over 45 mins. The mixture was stirred for 24 hrs at 110°C until the epoxy titration showed no epoxide

left. The material was cooled, filtered and the toluene was removed by vacuum distillation leaving a dark brown low viscosity liquid.

Example 4

5 To an Acryloid™ Coating Resin (acrylic ester polymers in an organic solvent solution) is added 2.5% by weight of the reaction product of Example 3.

Two piece clean aluminum cans are coated with the above mixture by dipping the cans into a vat containing the mixture.

10 The cans are dried, leaving a clear resistant coating on the metal surfaces of the cans. The coating has high gloss and is highly uniform, without discernable bubbles or pits.

Metalworking Lubricant Compositions:

15 Component B) is present in the metalworking lubricant compositions of the invention in a surfactant effective amount, which is usually in the range of from 0.001 to 10% by weight of the compositions, preferably from 0.1 to 3% by weight.

The branched reaction products (component B) used in the compositions of the invention are low-foaming surfactants, which can be used as the only surfactant in the compositions, or as a defoaming agent and/or surfactant in conjunction with other surfactants.

20 The metalworking lubricant compositions of the invention are referred to as "cutting fluids" when used in machine-tool operations to modify the harmful effects of friction and high temperatures. Their major function is to lubricate and cool. When cutting a screw thread, either on a lathe or with a tap, the lubricating function is most important; in production-grinding operations, the cooling function predominates. Lard oil has excellent lubricating qualities, but it tends to become rancid. Sulfurized mineral oil is one of the most popular cutting fluids. The sulfur tends to prevent chips from the workpiece from welding to the tip of the tool. For sawing and grinding operations, soluble oil, which is an oily emulsion freely miscible in water, is commonly used. Soluble oil, also called

emulsifying oil, is a milky emulsion containing e.g. sodium and potassium petroleum sulfonates.

Cutting fluids can be used in the operation of drilling machines, milling machines, turret lathes, grinding machines, power saws, presses, multiple-station vertical lathes, gang drills, production millers, gear-cutting machines, broaching machines, lapping and honing machines, boring machines, and the like. Also included is the cold forming of metal parts, such as cooking utensils, automobile bodies, and the like, which are carried out on punch presses.

Boundary lubricants are used where boundary conditions are encountered in metal forming processes in which the pressures required to deform the metal are too high to allow an oil film to form. In such applications, fatty oils, such as palm oil, or lubricants containing fatty materials are employed to reduce the friction and wear; the fatty acids react with the metal surface to form a tenacious soap film which provides lubrication up to temperatures near the melting point of the soap, usually about 250°F (120°C). Where conditions are not severe, long chain fatty alcohols can also act as boundary lubricants.

If the pressures and temperatures between contacting surfaces are moderate, the provision of a boundary lubricating film will suffice, whereas if conditions of both temperature and pressure are severe, some form of extreme pressure (EP) lubrication may be necessary.

Under the very severe conditions sometimes encountered in machining operations, it is necessary to prevent the chip from welding to the cutting tool, and only those compositions act as extreme pressure (EP) lubricants which contain, in addition to components A) and B), an additive as component C) which is a compound containing chemically active chlorine, sulfur, or phosphorus to form the corresponding iron chloride, sulfide, or phosphide, by instantaneous attack on the surface hot spots resulting from the collisions of surface asperities. The chemical stability of these so-called E.P. agents is designed to permit activity at the temperature near the rubbing surface, say 200°C and above, but not be corrosive under normal conditions, i.e. at ambient temperatures and pressures.

It should be noted that mixed film lubrication is almost invariably the true state of affairs when boundary and E.P. lubrication are encountered, i.e., an appreciable fraction of the load is carried by the fluid film in the "valleys" of the surface while the asperities in contact are permitted to carry the balance of the load

5 without seizure through the beneficent intervention of the boundary or EP lubricant. The very important break-in process of rubbing surfaces consists of the controlled reduction of the number and the size of the surface asperities so that fluid lubrication will prevail for most of the time.

The metalworking compositions of the invention can optionally

10 contain one or more of the following additives:

- D) a viscosity improver, e.g. a polymeric substance such as polybutene and copolymers of polymethacrylates.
- E) a pour-point depressant, e.g. a metallic soap, a condensation product of chlorinated wax and alkyl naphthalenes or phenols, polymethacrylates, and the like.
- F) an antioxidant, e.g. a hindered phenol such as dibutyl-p-cresol, amines such as phenyl- α -naphthylamine metal phenates which are alkaline earth salts of phenol disulfides, zinc salts of thiophosphates and carbamates, and the like.
- G) an amine such as an ethanolamine to provide alkalinity.
- H) a solvent, generally water.
- I) a buffer, e.g. boric acid.
- J) other nonionic surfactants.
- K) a corrosion inhibitor, e.g. tall oil fatty acid, octyl alcohol, and the like.
- L) a coupling agent, e.g. butoxyethanol, butyldiglycol, and the like.

The component A) lubricating agent is usually a mineral oil, such as a naphthenic oil, or an ester lubricating oil, although other lubricating agents described in the BACKGROUND OF THE INVENTION can also be used herein.

Component A) is usually present in from 30 to 90% by weight of the composition, preferably from 35 to 65% by weight.

In the component B) reaction products used in the metalworking compositions of the invention, the linking compound of formula I in component a) thereof is preferably epichlorohydrin or another epihalohydrin. However, trihaloalkanes can be used, such as 1,2,3-trichloropropane, 1,2,4-trichlorobutane, 1,3,6-trichlorohexane, and the like. Instead of chlorine in the epihalohydrins and trihaloalkanes, the corresponding bromine and iodine compounds can also be used, including compounds containing two or even all three of the above halogens.

The component b) compounds of formula II are organic (optionally alkoxyLATED) alcohols or the corresponding sulfhydryl or amine compounds.

The R² group can be a substituted or unsubstituted, saturated or unsaturated hydrocarbon group having from 1 to 36 carbon atoms. Examples of such hydrocarbon groups include linear or branched alkyl groups having from 1 to 36 carbon atoms, preferably from 4 to 22 carbon atoms, linear or branched alkenyl or alkynyl groups having from 2 to 36 carbon atoms, preferably from 4 to 22 carbon atoms, aryl groups having from 6 to 22 carbon atoms, and arenyl group having from 7 to 36 carbon atoms. Arenyl groups are alkyl-substituted aromatic radicals having a free valence at an alkyl carbon atom such as a benzylic group.

The R² group can also be a saturated carbocyclic group, an unsaturated carbocyclic group having one or more multiple bonds, a saturated heterocyclic group, or an unsaturated heterocyclic group having one or more multiple bonds. Any of the above R² groups can be substituted groups, i.e. the substituents can be single or multiple substituents such as a sulfur functionality such as a mercaptan or thio group; a nitrogen functionality such as an amine or amide functionality; an alcohol functionality, a silicon functionality, e.g., a siloxane; an ether functionality, e.g. a C₁-C₆ alkoxy group; or any combination thereof.

The R² group in formula II is preferably a branched chain alkyl group containing from 4 to 36 carbon atoms, preferably from 4 to 12 carbon atoms, and more preferably from 8 to 12 carbon atoms.

When the X group of formula II is an -S- group, the R² group will preferably have from 4 to 22 carbon atoms, examples of which include but are not limited to, dodecyl mercapto and 1-hexadecanethio.

When the R²X-group of formula II is a secondary or tertiary amino group, the group preferably contains from 4 to 22 carbon atoms, and n is preferably a number of from 1 to 50. Examples of primary and secondary amines useful for obtaining the R²X-group include, but are not limited to, dibutyl amine, cyclohexyl amine, isodecyl amine, and dioctylamine.

Optionally an additional component c) can be reacted with the linking agent of formula I and the compound of formula II. A glycidyl ether or amine can be added to the reaction of formula I and formula II. The amount of the glycidyl ether or glycidyl amine is from about 1 to about 20 mole percent based on the moles of the compounds of formula II used in the reaction. When the glycidyl ether or glycidyl amine is added, the ratio of component a) plus the glycidyl ether or glycidyl amine to component b) is preferably from about 1.2:1 to about 5:1. Examples of glycidyl ether include, but are not limited to, PEG 600 diglycidyl ether, TETRONIC™ 701 tetraglycidyl ether, triglycidyl di- or triethanolamine, polyoxyethylene (POE) 200 tallow amine diglycidyl ether, propoxylated (POP10) trimethylol propane triglycidyl ether, propoxylated (POP7) pentaerythritol tertraglycidyl ether. Examples of glycidyl amines include, but are not limited to, terfraglycidyl 1,6-hexane diamine, terfraglycidyl JEFFAMINE™ EDR-148, and terfraglycidyl isophorone diamine.

When Y in formula II is an amine or sulphydryl group, the resulting compounds can be readily prepared from the corresponding alcohols wherein the terminal hydroxy group is replaced by an -SH group or by an amine nitrogen. For example, a compound of formula II where Y is -OH can be subjected to a catalyzed ammoniation (with ammonia, or a lower alkylamine) for replacement of the hydroxyl.

In the compounds of formula II, the AO groups when present are preferably all ethyleneoxy groups. However, as stated above, each OA group can be

independently an ethyleneoxy (EO), 1,2-propyleneoxy (PO), or 1,2-butyleneoxy (BO) group, i.e. any one or more of such groups can be present, and they can be present in any order, as well as be present in blocks, e.g. compounds of formula III:



- 5 wherein R^2 has the meaning given above, m is a number of from 0 to 100, preferably from 1 to 50, p is a number of from 0 to 50, e.g. from 1 to 50, and q is a number of from 0 to 50, e.g. from 1 to 50. Compounds of formula III in which R^2 is a branched chain alkyl group having from 4 to 12 carbon atoms, m is a number of from 2 to 20, and p and q are 0 are preferred.

10 The degree of hydrophilic and hydrophobic properties of the reaction products of components a) and b) can be readily controlled by controlling the type and number of alkyleneoxy groups in component b). For example, the greater the number of ethyleneoxy groups present, the greater the water solubility, while the presence of 1,2-propyleneoxy groups and/or 1,2-butyleneoxy groups for example, 15 will decrease water solubility.

In general, the compounds of formula III wherein the sum of n, m, and p is at least 1, and especially at least 2 are preferred for use herein.

The branched reaction products used in the practice of the invention can be prepared by reacting components a) and b) (and c) if present) together, 20 preferably in the presence of an inert organic solvent, preferably a solvent such as toluene that will azeotrope water, and in the presence of an inorganic base such as an alkali metal hydroxide, e.g. aqueous sodium hydroxide or potassium hydroxide, at a temperature in the range of from 60 to 125°C. In a preferred embodiment of the process, component b) is first mixed with the base, and the organic solvent, if 25 present, and water is removed, e.g. by azeotropic distillation. Then component a) (and c), if present) is slowly added and the reaction continued until the reaction is completed. The reaction mixture is filtered and the filtrate vacuum stripped to remove any organic solvent.

Inert organic solvents that can be used in the above process are 30 nonmiscible with water and nonhydroxylic. Examples of such solvents include

toluene, CHCl_3 , CH_2Cl_2 , chlorobenzene, acetonitrile, and petroleum ethers, preferably toluene.

The invention will be illustrated but not limited by the following examples.

5

EXAMPLES

Example 1

Preparation of the reaction product of decyl alcohol - 4EO and epichlorohydrin

About 150 grams of decyl alcohol ethoxylated with an average of 4 moles of ethylene oxide (0.45 OH equivalents) were mixed with 385 grams of toluene and 54 grams of 50% aq. NaOH (0.675 equivalents). The water was removed by azeotropic distillation and when a moisture level of less than 0.8% was reached, about 46 grams (0.51 equivalents) of epichlorohydrin were slowly added. This mixture was allowed to react at 100-110°C for 24 hours. An aliquot of this mixture was removed and filtered to remove the NaCl and vacuum stripped to 15 remove the toluene to give an amber, easily pourable liquid product that was dispersible in water.

Example 2

Two water-miscible metalworking fluid concentrates are prepared by mixing together the following components shown in Table 1 below. The emulsifier pre-mixes are prepared first, and then mixed with either a mineral oil or an ester oil shown in Table 1 below.

Emulsifier Pre-mix

TABLE 1

		Mineral Oil	Ester
Raw Material	Functions	%	%
Monoethanolamine	Alkalinity	15.6	15.0
Triethanolamine	Alkalinity	3.1	1.3
Boric Acid	Buffer System, Biostability	7.8	3.1
Deionized Water	Solvent	8.2	1.6
Tall Oil Fatty Acid 25/30	Corrosion Inhibitor, Anionic Emulsifier	28.6	15.0
LOROL® C8-98 ¹	Corrosion Inhibitor, Anionic Emulsifier	-	6.0
EUMULGIN® 3499 ²	Corrosion Inhibitor, Coupling Agent	7.1	11.0
EUMULGIN® 3370V ³	Nonionic Surfactant	7.2	17.0
EUMULGIN® EP5LV ⁴	Nonionic Surfactant	14.3	16.0
Butoxyethanol	Coupling Agent	7.1	-
Butyldiglycol	Coupling Agent	-	11.0
Example 1 Reaction Product	Wetting Agent, Defoaming Agent, Dispersing Agent, Lubricant Enhancer, Extreme Pressure Agent	3.0	3.0
Appearance		Clear Liquid	Clear Liquid
Soluble Oil			
Emulsifier Pre-Mix		50.0	40.0
Naphthenic Oil	Base Oil	50.0	-
EDENOR® EHO ⁵	Base Oil, Lubricity	-	60.0

- 5 1- Octyl alcohol
 2- A proprietary emulsifier blend
 3- Ethoxylated cetyl/oleyl alcohol
 4- Ethoxylated cetyl/oleyl alcohol with SEO groups
 5- a lubricating ester oil

10 For commercial purposes, it is desirable to add additional components to the above metal working fluids, e.g. copper corrosion inhibitors, biocides, and fungicides.

The above metalworking fluid concentrates can be mixed with water to form a metalworking lubricant composition for use in the working of metals, e.g. a 3% solution in water.

Example 3

Preparation of the reaction product of octyl alcohol · 4EO and epichlorohydrin

About 200.0 gm (0.654 hydroxyl equivs.) of octyl alcohol ethoxylated with an average of 4 moles of ethylene oxide was mixed with 400 gm toluene and 78.4 gm (0.98 equivs.) of 50% NaOH. Water was removed by azeotropic distillation until the level was below 0.8%. The mixture was cooled to 80°C. and 67.2 gm (0.72 moles) of epichlorohydrin was added over 45 mins. The mixture was stirred for 24 hrs at 110°C. until the epoxy titration showed no epoxide left. The material was cooled, filtered and the toluene was removed by vacuum distillation leaving a dark brown low viscosity liquid.

Example 4

Two water-miscible metalworking fluid concentrates are prepared by mixing together the following components set forth in Table 2 below.

15

TABLE 2

Metalworking Fluid Concentrate	Mineral Oil - Based	Ester - Based
	%	%
Monoethanolamine	8.3	5.7
Triethanolamine	1.6	0.6
Boric Acid	3.9	1.4
Deionized Water	3.4	0.7
Tall Oil Fatty Acid (25/30)	12.7	4.3
LOROL® C8 98	-	2.5
EUMULGIN® 3499	4.0	5.7
EUMULGIN® 3412V ⁶	6.6	6.5
EUMULGIN® ET 5V ⁷	-	6.4
EUMULGIN® EP 5 LV	5.0	-
2-Butoxyethanol	2.5	-
Butyldiglycol	-	4.2
Naphthenic Oil	50.0	-
EDENOR® EHO	-	60.0
Example 3 Reaction Product	2.0	2.0
Appearance	Clear Liquid	Clear Liquid

6- an ethoxylated alcohol

7- Ethoxylated cetyl/stearyl alcohol (5EO groups)

The above concentrate can be diluted to a 3% concentration in water for use in metalworking. In addition to the above components, it is desirable to also include copper corrosion inhibitors, biocides, and fungicides.

Compositions for Electroplating and Electrowinning:

5 The branched reaction products (component B)) used in the aqueous compositions of the invention are low foaming surfactants, which can be used as the only surfactant in the aqueous compositions, or as a defoaming agent and surfactant in conjunction with other surfactants.

10 Component B) is present in the aqueous compositions of the invention in a surfactant effective amount, which is usually in the range of from 0.001 to 5% by weight of the compositions, preferably from 0.1 to 3% by weight.

15 The component A) metals or metalloids can be one or more of zinc, nickel, copper, chromium, manganese, iron, cobalt, gallium, germanium, arsenic, selenium, ruthenium, rhodium, palladium, silver, cadmium, indium, tin, lead, bismuth, mercury, antimony, gold, iridium, and platinum. The above metals or metalloids can be added to the aqueous compositions in metallic form and/or in the form of anions.

20 In addition to the metals listed above, many alloys are commercially electroplated, such as brass, bronze, many gold alloys, lead-tin, nickel-iron, nickel-cobalt, nickel-phosphorous, tin-nickel, tin-zinc, zinc-nickel, zinc-cobalt, and zinc-iron. Electroplated alloys in lesser use include lead-indium, nickel-manganese, nickel-tungsten, palladium alloys, silver alloys, and zinc-manganese.

25 Another type of electrodeposit in commercial use is the composite form, in which insoluble materials are codeposited along with the electrodeposited metal or alloy to produce particular desirable properties. Polytetrafluoroethylene (PTFE) particles are codeposited with nickel to improve lubricity. Silicon carbide and other hard particles including diamond are co-deposited with nickel to improve wear properties or to make cutting and grinding tools.

The term "metalloid" is to be understood to mean nonmetals which are semiconductors, e.g. arsenic, germanium, and the like, which can be electroplated in the same manner as metals.

The essential components of an electroplating process are an electrode to be plated (the cathode); a second electrode to complete the circuit (the anode); an electrolyte containing the metal ions to be deposited; and a d-c power source. The electrodes are immersed in the electrolyte such that the anode is connected to the positive leg of the power supply and the cathode to the negative. As the current is increased from zero, a minimum point is reached where metal plating begins to take place on the cathode.

There are a number of electroplating methods for which the compositions of the invention can be used. Materials such as strip steel can be plated in plating tanks where coils of steel are unrolled on a continuous basis, fed through a series of preparation steps, and then into the plating tank. To electroplate wire, the wire is uncoiled from spools or reels, passed through processing steps and then plated as individual strands. Wire is plated commercially with metals such as copper, copper alloys, zinc, iron, iron alloys, nickel, nickel alloys, gold, and silver. Stampings, moldings and castings are typically mounted onto specially designed plating racks. Bulk plating methods can be used for small parts, e.g. dipping baskets and plating barrels made of inert plastic materials. Where parts are large and only smaller areas of the parts are to be plated, brush plating is used, i.e. using plating tools which are shaped anode materials covered with an absorbent material saturated with the plating solution.

Plating tanks are formed from materials which are either totally inert to the plating solution or are lined with inert materials to protect the tank. For alkaline plating solutions, mild steel materials are used. For acid plating solutions other materials are used, depending on the chemical composition of the plating bath, such as titanium and various stainless steel alloys, polytetrafluoroethylene, KARBATE®, HASTALLOYS®, zirconium alloys, and the like.

The plating tanks are fitted for d-c power, usually with round copper busbars. Filters are usually present to remove fine particulate matter. Heating or cooling units may be present, such as heating coils or cooling water coils. Two types of anodes can be used, i.e. soluble or insoluble.

Soluble anodes are designed to dissolve effectively with current flow and preferably, not to dissolve when the system is idle. A plating solution having the anode efficiency close to the cathode efficiency provides a balanced process that has fewer control problems and is less costly. If the anode efficiency is much greater than the cathode efficiency and there are only small solution losses, the dissolved metal concentration rises until at some time the bath has to be diluted back or the excess metal has to be reduced by some other means. If the anode efficiency is less than the cathode efficiency, the dissolved metal decreases, pH decreases, and eventually metal salt additions and other solution corrections are required. Based on the cost of metal, it is usually considerably more economical to plate from the anode rather than add metal salt. (See e.g. Kirk-Othmer, Encyclopedia of Chemical Technology, 4th Edition under the heading Electroplating).

Insoluble anodes are used exclusively in some plating baths. Chromium plating solutions utilize lead-tin, lead-antimony, or lead anodes. Gold and other precious metal plating processes use stainless steel anodes, keeping inventory costs down.

Whenever insoluble anodes are used, the pH of the plating solution decreases along with the metal ion concentration. In some plating baths, a portion of the anodes is replaced with insoluble anodes in order to prevent metal ion buildup or to reduce metal ion concentration.

The use of insoluble anodes can also result in side effects. In alkaline cyanide solutions, the generation and buildup of carbonates is accelerated remarkably, along with a significant reduction in alkalinity. In acid solutions the pH decreases as well, requiring frequent adjustments. In sulfamate nickel plating solutions, insoluble anodes, and even slightly passive soluble anodes, partially

oxidize the sulfamate ion to form sulfur-bearing compounds which change the character and performance of the deposit (See Kirk-Othmer, *supra*).

The substrates being electroplated must usually be prepared prior to electroplating. Because electroplating takes place at the exact molecular surface of a work, it is important that the substrate surface be absolutely clean and receptive to the plating. In the effort to get the substrate into this condition, several separate steps may be required, such as soak cleaning, followed by electrocleaning, followed by rinsing.

Formulations of plating baths can be flexible in some systems and very sensitive to variations in others. Many of the more recent changes have resulted from waste treatment and safety requirements. Besides the ability to deposit a coating having acceptable appearance and physical properties, the desired properties of a plating bath would include: high metal solubility, good electrical conductivity, good current efficiencies for anode and cathode, noncorrosivity to substrates, nonfuming, stable, low hazard, low anode dissolution during down-time, good throwing power, good covering power, wide current density plating range, ease of waste treatment, and economical to use. Few formulas have all these attributes. Only a few plating solutions are commercially used without special additives, but chemical costs often constitute a relatively low percentage of the total cost of electroplating. Additives are used to brighten, reduce pitting, or otherwise modify the character of the deposit or performance of the solution. Preferred formulations are normally specified by the suppliers of the proprietary additives.

Purification, often needed once a plating bath is made, is used periodically to maintain the plating solutions. Alkaline zinc plating solutions are sensitive to a few mg/L of heavy-metal contamination, which can be precipitated using sodium sulfide and filtered out. Nickel plating solutions may contain excess iron and unknown organic contaminants. Iron is removed by peroxide oxidation, precipitation at a pH of about 5, then filtered out. The more complex, less water-soluble organic contaminants along with some trace metals are removed with activated carbon treatments in separate treatment tanks.

Another common purification treatment used both on new and used plating solution is dummying. Heavy-metal impurities are removed by electrolyzing, usually at low current densities, using large disposable steel cathodes. Good agitation and lower pH speed the process.

5 Analysis and testing are required whenever a new plating solution is made up, and thereafter at periodic intervals. The analyses are relatively simple and require little equipment. Trace metal contaminants can be analyzed by using spot tests, colorimetrically, and with atomic absorption spectrophotometry. Additives, chemical balance, impurity effects, and many other variables are tested with small
10 plating cells, such as the Hull cell.

The precise makeup of plating bath compositions depends on the metal being plated. For example, alkaline cadmium plating baths usually contain cyanide salts, such as sodium cyanide, while acidic baths contain an acid, usually sulfuric acid. Various additives may also be present.

15 Cyanide copper plating baths typically contain copper metal, copper cyanide, potassium cyanide, potassium hydroxide, Rochelle salts, and sodium carbonate. Acid copper plating baths typically contain copper metal, copper sulfate, sulfuric acid, and additives.

20 Watts nickel plating baths typically contain nickel metal, nickel sulfate, nickel chloride, boric acid, and additives. Sulfamate nickel plating baths contain nickel sulfamate instead of nickel sulfate.

Silver plating baths typically contain silver cyanide, potassium cyanide, potassium carbonate, and sometimes potassium nitrate and potassium hydroxide, plus additives.

25 Zinc plating baths can range from simple zinc sulfate solutions to zinc plus chloride/boric acid baths with brighteners and wetting agents. Also, zincate baths and cyanide baths are also used.

Electroforming is the production or reproduction of articles by
30 electrodeposition upon a mandrel or mold that is subsequently separated from the deposit. The separated electrodeposit becomes the manufactured article. Of all the

metals, copper and nickel are most widely used in electroforming. Mandrels are of two types: permanent or expendable. Permanent mandrels are treated in a variety of ways to passivate the surface so that the deposit has very little or no adhesion to the mandrel, and separation is easily accomplished without damaging the mandrel.

- 5 Expendable mandrels are used where the shape of the electroform would prohibit removal of the mandrel without damage. Low melting alloys, metals that can be chemically dissolved without attack on the electroform, plastics that can be dissolved in solvents, are typical examples.

Electrowinning is used in the process of recovering metals from ores.

- 10 The aqueous processes for electrowinning of metals from ores have the following common unit operations or steps: (1) the metal in the ore is converted to an acid-soluble form and this may be an oxidizing roast or a reduction; (2) ores from step 1 are leached, usually in sulfuric acid; (3) metal solutions from step 2 are purified and in some cases concentrated; (4) purified metal solutions are electrolyzed in cells
15 where the metal is deposited on the cathode; and (5) acid is produced at the anode and recycled to the leaching step 2. Some acid values are lost, usually in the purification step 3. Makeup acid is added in the leaching step 2. In most cases the metal solution from leaching step 2 contains impurities, other metals. Many of these metals have the characteristics of low hydrogen over-voltage. Codeposition of the
20 impurity metals causes contamination of the desired product and decreases current efficiencies. The removal of impurities before electrolysis is very important. This is especially true in the case of the more reactive metals such as zinc, and manganese. These metals have deposition potentials close to the hydrogen evolution potential.
The current efficiency of manganese electrowinning is about 60 to 68%. The
25 principal inefficiency is hydrogen evolution.

- The electrowinning of metals from aqueous solutions is generally carried out in tank cells. Developments in the electrowinning of metals from aqueous solutions have been directed toward improved anodes, improved additives, higher current densities, the use of ion-exchange membranes, better electrolyte
30 quality control, and computer modeling of the processes.

Another electroplating process in which the component B) branched reaction products used in the aqueous compositions of the invention can be employed is the electrochemical treatment of waste solutions containing dissolved metals.

5 It is to be understood that the term "electroplating composition" used in the claims includes electroplating compositions, electroforming compositions, electrowinning compositions, and waste solutions containing dissolved metals.

It is also understood that the component A) metals and metalloids can be present in ionic form and/or in elementary form.

10 In the component B) branched reaction products used in the aqueous compositions of the invention, the linking compound of formula I in component B)a) is preferably epichlorohydrin or another epihalohydrin. However, trihaloalkanes can be used, such as 1,2,3-trichloropropane, 1,2,4-trichlorobutane, 1,3,6-trichlorohexane, and the like. Instead of chlorine in the epihalohydrins and 15 trihaloalkanes, the corresponding bromine and iodine compounds can also be used, including compounds containing two or even all three of the above halogens.

The component B)b) compounds of formula II are organic (optionally alkoxylated) alcohols or the corresponding sulfhydryl or amine compounds.

20 The R² group can also be a substituted or unsubstituted, saturated or unsaturated hydrocarbon group having from 1 to 36 carbon atoms. Examples of such hydrocarbon groups include linear or branched alkyl groups having from 1 to 36 carbon atoms, preferably from 4 to 22 carbon atoms, linear or branched alkenyl or alkynyl groups having from 2 to 36 carbon atoms, preferably from 4 to 22 carbon atoms, aryl groups having from 6 to 22 carbon atoms, and arenyl groups having from 7 to 36 carbon atoms. Arenyl groups are alkyl-substituted aromatic radicals having a free valance at an alkyl atom such as a benzylic group.

25 The R² group can be a saturated carbocyclic group, an unsaturated carbocyclic group having one or more multiple bonds, a saturated heterocyclic group, or an unsaturated heterocyclic group having one or more multiple bonds.

30 Any of the above R² groups can be substituted groups, i.e. the substituents can be

single or multiple substituents such as a sulfur functionality such as a mercaptan or thio group; a nitrogen functionality such as an amine or amide functionality; an alcohol functionality, a silicon functionality, e.g., a siloxane; an ether functionality, e.g. a C₁-C₆ alkoxy group; or any combination thereof.

5 The R² group in formula II is preferably a branched chain alkyl group containing from 4 to 36 carbon atoms, preferably from 4 to 12 carbon atoms, and more preferably from 8 to 12 carbon atoms.

10 When the X group of formula II is an -S- group, the R² group will preferably have from about 4 to about 22 carbon atoms, examples of which include but are not limited to, dodecyl mercapto and 1-hexadecanethio.

15 When the R²X-group of formula II is a secondary or tertiary amino group, the group preferably contains from 4 to 22 carbon atoms, and n is preferably a number of from 1 to 50. Examples of primary and secondary amines useful for obtaining the R²X-group include, but are not limited to, dibutyl amine, cyclohexyl amine, isodecyl amine, and dioctylamine.

20 Optionally, an additional component B)c) can be reacted with the linking agent of formula I and the compound of formula II. A glycidyl ether or amine can be added to the reaction of formula I and formula II. The amount of the glycidyl ether or glycidyl amine is from about 1 to about 20 mole percent based on the moles of the compounds of formula II used in the reaction. When the glycidyl ether or glycidyl amine is added, the ratio of component B)a) plus the glycidyl ether or glycidyl amine to component B)b) is preferably from about 1.2:1 to about 5:1. Examples of glycidyl ether include, but are not limited to, PEG 600 diglycidyl ether, TETRONIC™ 701 tetraglycidyl ether, triglycidyl di or triethanolamine, 25 polyoxyethylene (POE) 200 tallow-amine diglycidyl ether, propoxylated (POP10) trimethylol propane triglycidyl ether, propoxylated (POP7) pentaerythritol tertraglycidyl ether. Examples of glycidyl amines include, but are not limited to, tetraglycidyl 1,6-hexane diamine, tetraglycidyl JEFFAMINE™ EDR-148, and tetraglycidyl isophorone diamine.

When Y in formula II is an amine or sulfhydryl group, the resulting compounds can be readily prepared from the corresponding alcohols wherein the terminal hydroxy group is replaced by an -SH group or by an amine nitrogen. For example, a compound of formula II where Y is -OH can be subjected to a catalyzed ammoniation (with ammonia, or a lower alkylamine) for replacement of the hydroxyl. In the compounds of formula II, the AO groups when present are preferably all ethyleneoxy groups. However, as stated above, each OA group can be independently an ethyleneoxy (EO), 1,2-propyleneoxy (PO), or 1,2-butyleneoxy (BO) group, i.e. any one or more of such groups can be present, and they can be present in any order, as well as be present in blocks, e.g. compounds of formula III:



wherein R² has the meaning given above, m is a number of from 0 to 100, preferably from 1 to 50, p is a number of from 0 to 50, e.g. from 1 to 50, and q is a number of from 0 to 50, e.g. from 1 to 50. Compounds of formula III in which R² is a branched chain alkyl group having from 4 to 12 carbon atoms, m is a number of from 2 to 20, and p and q are 0 are preferred.

The degree of hydrophilic and hydrophobic properties of the reaction products of components B)a) and B)b) can be readily controlled by controlling the type and number of alkyleneoxy groups in component B)b). For example, the greater the number of ethyleneoxy groups present, the greater the water solubility, while the presence of 1,2-propyleneoxy groups and/or 1,2-butyleneoxy groups for example, will decrease water solubility.

In general, the compounds of formula III wherein the sum of m, p, and q is at least 1, and especially at least 2 are preferred for use herein.

The branched reaction products used in the practice of the invention can be prepared by reacting components B)a) and B)b) (and B)c), if present) together, preferably in the presence of an inert organic solvent, preferably a solvent such as toluene that will azeotrope water, and in the presence of an inorganic base such as an alkali metal hydroxide, e.g. aqueous sodium hydroxide or potassium hydroxide, at a temperature in the range of from 60 to 125°C. In a preferred

embodiment of the process, component B)b) is first mixed with the base, and the organic solvent, if present, and water is removed, e.g. by azeotropic distillation.

Then component B)a) (and B)c), if present) is slowly added and the reaction continued until the reaction is completed. The reaction mixture is filtered and the

5 filtrate vacuum stripped to remove any organic solvent.

Inert organic solvents that can be used in the above process are nonmiscible with water and nonhydroxylic. Examples of such solvents include toluene, CHCl₃, CH₂Cl₂, chlorobenzene, acetonitrile, and petroleum ethers, preferably toluene.

10 This invention will be illustrated but not limited by the following examples.

EXAMPLES

Example 1

Preparation of the reaction product of decyl alcohol · 4EO and epichlorohydrin

15 About 150 grams of decyl alcohol ethoxylated with an average of 4 moles of ethylene oxide (0.45 OH equivalents) were mixed with 385 grams of toluene and 54 grams of 50% aq. NaOH (0.675 equivalents). The water was removed by azeotropic distillation and when a moisture level of less than 0.8% was reached, about 46 grams (0.51 equivalents) of epichlorohydrin were slowly added.

20 This mixture was allowed to react at 100°-110°C for 24 hours. An aliquot of this mixture was removed and filtered to remove the NaCl and vacuum stripped to remove the toluene to give an amber, easily pourable liquid product that was dispersible in water.

Example 2

25 An aqueous copper plating bath is formulated with the following components:

<u>Component</u>	<u>Concentration, g/l</u>
Cu metal	57
CuSO ₄ .5H ₂ O	225
H ₂ SO ₄	60
Cl ⁻	0.5
reaction product of Ex.1	0.2

5

The above plating bath has a pH of less than 0. Nonetheless, the reaction product of Example 1 is stable in this bath at typical plating temperatures, e.g. 25°C. The above bath can be used for electroplating, electrowinning, and electroforming.

10

Example 3

Preparation of the reaction product of octyl alcohol - 4EO and epichlorohydrin

About 200.0 gm (0.654 hydroxyl equivs.) of octyl alcohol ethoxylated with an average of 4 moles of ethylene oxide was mixed with 400 gm toluene and 78.4 gm (0.98 equivs.) of 50% NaOH. Water was removed by azeotropic distillation until the level was below 0.8%. The mixture was cooled to 80°C. and 67.2 gm (0.72 moles) of epichlorohydrin was added over 45 mins. The mixture was stirred for 24 hrs at 110°C until the epoxy titration showed no epoxide left. The material was cooled, filtered and the toluene was removed by vacuum distillation leaving a dark brown low viscosity liquid.

15

20

Example 4

An aqueous acidic nickel plating bath is formulated with the following components:

25

30

<u>Component</u>	<u>Concentration, g/l</u>
Ni metal	82
NiSO ₄ .6H ₂ O	300
NiCl ₂ .6H ₂ O	60
H ₃ BO ₃	40
reaction product of Ex. 3	0.15

Latex Compositions:

In the above compounds of component A), the linking compound of formula I is preferably epichlorohydrin or another epihalohydrin. Also,

trihaloalkanes can be used, such as 1,2,3-trichloropropane, 1,2,4-trichlorobutane, 1,3,6-trichlorohexane, and the like. Instead of chlorine in the epihalohydrins and the trihaloalkanes, the corresponding bromine and iodine compounds can also be used, including compounds containing two or even all three of the above halogens.

5 The component B) compounds of formula II are organic (optionally alkoxylated) alcohols or the corresponding sulphydryl or amine compounds.

The R² group can be a substituted or unsubstituted, saturated or unsaturated hydrocarbon group having from 1 to 36 carbon atoms. Examples of such hydrocarbon groups include linear or branched alkyl groups having from 1 to 10 36 carbon atoms, preferably from 4 to 22 carbon atoms, linear or branched alkenyl or alkynyl groups having from 6 to 22 carbon atoms, and arenyl groups having from 7 to 36 carbon atoms. Arenyl groups are alkyl-substituted aromatic radicals having a free valance at an alkyl carbon atom such as a benzylic group.

15 The R² group can also be a saturated carbocyclic group, an unsaturated carbocyclic group having one or more multiple bonds, a saturated heterocyclic group, or an unsaturated heterocyclic group having one or more multiple bonds. Any of the above R² groups can be substituted groups, i.e. the groups can be single or multiple substituents such as one or more halogen substituents, for example, Cl, Fl, I, and Br; a sulfur functionality such as a mercaptan 20 or thio group, a nitrogen functionality such as an amine or amide functionality; an alcohol functionality, a silicon functionality, e.g., a siloxane; an ether functionality, e.g. a C₁-C₆ alkoxy group; or any combination thereof.

The R² group in formula II is preferably a branched chain alkyl group containing from 4 to 36 carbon atoms, preferably from 4 to 12 carbon atoms, and 25 more preferably from 8 to 10 carbon atoms.

When the X group of formula II is an -S- group, the R² group will preferably have from about 4 to about 22 carbon atoms, examples of which include but are not limited to, dodecyl mercapto and 1-hexadecanethio.

When the R²X-group of formula II is a secondary or tertiary amino 30 group, the group preferably contains from 4 to 22 carbon atoms, and n is preferably

a number of from 1 to 50. Examples of primary and secondary amines useful for obtaining the R^2X - group include, but are not limited to, dibutyl amine, cyclohexyl amine, isodecyl amine, and dioctylamine.

- Optionally an additional component C) can be reacted with the
- 5 linking agent of formula I and the compound of formula II. A glycidyl ether or amine can be added to the reaction of formula I and formula II. The amount of the glycidyl ether or glycidyl amine is from about 1 to about 20 mole percent based on the moles of the compounds of formula II used in the reaction. When the glycidyl ether or glycidyl amine is added, the ratio of component A) plus the glycidyl ether or
10 glycidyl amine to component B) is preferably from about 1.2:1 to about 5:1.
- Examples of glycidyl ether include, but are not limited to, PEG 600 diglycidyl ether, TETRONIC™ 701 tetraglycidyl ether, triglycidyl di- or triethanolamine, polyoxyethylene (POE) 200 tallow amine diglycidyl ether, propoxylated (POP10) trimethylol propane triglycidyl ether, propoxylated (POP7) pentaerythritol
15 tetraglycidyl ether. Examples of glycidyl amines include, but are not limited to, tetraglycidyl 1,6-hexane diamine, tetraglycidyl JEFFAMINE™ EDR-148, and tetraglycidyl isophorone diamine.

When Y in formula II is an amine or sulfhydryl group, the resulting compounds can be readily prepared from the corresponding alcohols wherein the
20 terminal hydroxy group is replaced by an -SH group or by an amine nitrogen. For example, a compound of formula II where Y is -OH can be subjected to a catalyzed ammoniation (with ammonia, or a lower alkylamine) for replacement of the hydroxyl.

In the compounds of formula II, the AO groups when present are
25 preferably all ethyleneoxy groups. However, as stated above, each OA group can be independently an ethyleneoxy (EO), 1,2-propyleneoxy (PO), or 1,2-butyleneoxy (BO) group, i.e. any one or more of such groups can be present, and they can be present in any order, as well as be present in blocks, e.g. compounds of formula III:



wherein R² has the meaning given above, m is a number of from 0 to 100, preferably from 1 to 50, p is a number of from 0 to 50, e.g. from 1 to 50, and q is a number of from 0 to 50, e.g. from 1 to 50. Compounds of formula III in which R² is a branched chain alkyl group having from 4 to 12 carbon atoms, m is a number of from 2 to 20, and p and q are 0 are preferred.

The degree of hydrophilic and hydrophobic properties of the reaction products of components A) and B) can be readily controlled by controlling the type and number of alkyleneoxy groups in component B). For example, the greater the number of ethyleneoxy groups present, the greater the water solubility, while the presence of 1,2-propyleneoxy groups and/or 1,2-butyleneoxy groups for example, will decrease water solubility.

In general, the compounds of formula III wherein the sum of n, m, and p is at least 1, and especially at least 2 are preferred for use herein.

The above reaction products can be prepared by the process disclosed in U.S. 5,827,453, the disclosure of which is expressly incorporated herein by reference.

In general, the component A) and B) (and C) if present) reactants are reacted together, preferably in the presence of an inert organic solvent such as toluene that will azeotrope water, and in the presence of a base, such as aqueous sodium hydroxide, at a temperature of from 60° to 125°C. Preferably component B) is first mixed with the base and the organic solvent, and water is removed by azeotropic distillation. Then component A) (and C) if present) is slowly added and the reaction continued until the reaction is completed. The reaction mixture is filtered and vacuum stripped to remove the organic solvent.

The above Component II) reaction products are readily soluble in the aqueous latex compositions; are both surfactants and defoaming agents; are highly stable yet readily biodegradable; and in addition possess all of the advantages discussed above, e.g. they do not destabilize the latex compositions; they do not interfere with dipping or coating or other procedures; they defoam the latex compositions so effectively that no holes are present in the resulting articles; they

are highly effective wetting agents; they are compatible with soap and other surfactants; and they are stable under a wide range of processing conditions including temperature stability.

In natural rubber latex technology, which includes natural rubber latex from rubber trees, and aqueous finely divided dispersions from solid natural rubbers, materials to be added to the rubber are colloidally dispersed in water and mixed into the latex, a process involving the use of lighter equipment and less power than the mixing of solid rubber compounds. The latex compound can then be used in a variety of processes such as coating or impregnating of cords, fabrics, or paper; in adhesives; molding (such as in toys); dipping (for thin articles like balloons, or household and surgeon's gloves); rubber thread (for garments); and production of foam. Latex technology is particularly important in producing articles for medical and surgical uses, such as latex gloves and other medical and surgical articles.

Natural rubber latex is a milky white liquid emulsion found in the cells of flowering plants such as the Para rubber tree (*Hevea brasiliensis*). It is also produced by the cells of plants of the family Asclepiadaceae but also by those in the families Apocynaceae, Sapotaceae, Euphorbiaceae, Papaveraceae, Moraceae, and Asteraceae (Compositae). The latex circulates in branched tubes that penetrate the tissues of the plant in a longitudinal direction, conducting substances and acting as an excretory reservoir.

Latex represents rubber in its most tractable form. Concentration of latex to a content of 60 to 70 percent dry rubber is performed either at the source or in the user country by means of centrifuging, evaporation, or a process known as creaming, in which an agent is added to the latex that causes the rubber particles to swell and rise to the surface of the liquid.

Latex is an excellent adhesive and is widely used in its natural state, but for most industrial uses it needs additives and vulcanization. Accelerating agents for vulcanizing and other essential fillers are added. One of the oldest uses of latex is in the production of such dipped goods as rubber gloves and prophylactics.

The process consists of dipping formers of the correct size and shape into compounded latex, then drying, repeating the operations, and vulcanizing.

Rubber (elastic) thread also is produced from latex. Initially, strips were cut from a thin sheet to form a thread of square cross section. Later, the much superior round thread was obtained by extruding compounded latex into a bath of coagulant through glass nozzles.

Foam rubber has been one of the most important latex products since its discovery in the 1920s. The confinement of thousands of gaseous bubbles in natural rubber cells provides ideal resilience. In the simple manufacturing process, excess ammonia is removed from the latex, and after a vigorous stirring with dispersions of soap, sodium fluorosilicate is added to the frothy mixture as a gelling agent, along with accelerating agents, zinc oxide, and antioxidant. After the liquid has stood in a mold for several minutes to permit gelling, it is vulcanized. In practice, the process requires the most careful control and the judgment of experienced personnel.

Foam products were made originally in individual molds which progressed along a conveyor in series and into each of which a predetermined quantity of foam was inserted, the mold closing during its progress to the oven. Washing, drying, and finishing completed the process. For large-scale production, a new method has supplanted this early method, which is still in active service. The process consists of filling a fixed mold with a metered quantity of foam, sealing it with its lid, and evacuating the air; the foam expands to partly fill the resulting vacuum, and then is frozen; next, carbon dioxide gas is passed in to fill the remaining vacuum in the foam, and the temperature is raised to 104°C (219°F) for curing.

The carpet industry has made increasing use of latex not only as a separate foam rubber underlay but as an undercoating on the carpet itself and as an anchoring matrix for tufted carpets.

Foams may also comprise a blend of natural and styrene-butadiene rubbers, the latter reducing the cost with some reduction in resilience.

Vulcanization is usually the last step in preparing a final product. It gives strength, hardness, and elasticity to rubber by treating it with heat and vulcanizing agents, such as sulfur. During vulcanization, the heat causes the sulfur to combine with the rubber and cure it. This makes the rubber stronger and more durable. Generally, the more sulfur that is added, the firmer the vulcanized compound will be. Vulcanization may take from a few minutes to several hours.

Manufacturers vulcanize and shape molded products at the same time by heating the molds under pressure. They vulcanize extruded and sheet products on pans in hot-air or steam chambers. Dipped products are vulcanized in hot water, 10 hot air, or open steam while still on the molds. Foam products in their molds are vulcanized in steam chambers or in boiling water.

One or more additives that can be added to natural rubber latex, in addition to component II) above, include inorganic sulfur for vulcanization, clay fillers, molten resins, zinc oxide (used to absorb evolved hydrochloric acid), silica, 15 accelerators such as aldehyde-amines, guanidines, thiuram sulfides, thiazoles, thiazolines, dithiocarbamates, and mercaptoimidazolines, light process oil free from polyacrylic aromatics, other mineral fillers in addition to or instead of clay, plasticizers such as elastic plasticizers, strong acid soaps, sodium or potassium salts of rosin acids, and the like.

20 Other vulcanizing agents that can be used in place of inorganic sulfur include oxidizing agents such as selenium, tellurium, organic peroxides, and nitro compounds, and also generators of free radicals, such as organic peroxide, and azo compounds. In addition, sulfur-containing compounds such as dimorpholinyl disulfide and tetraethylthiuram disulfide can be used as vulcanizing agents and 25 which also function as accelerators.

Antioxidants can also be added, including highly hindered phenols, obtained by alkylation of phenols or cresols, and derivatives of aromatic phosphite esters.

Also, antiozonates can be added, such as p-phenylenediamines e.g. N,N¹-dialkyl-p-phenylenediamines, and the condensation products of amines and ketones.

- Vulcanization retarders can be present, such as organic acids and
5 anhydrides, cyclohexylthio-phthalimide, and sulfenamides.

Moreover, while natural rubber latex normally contains fatty acids or their soaps, it is sometimes necessary to add more.

- All of the above additives are known additives (except of course component II of the present latex compositions) and one or more thereof can be
10 added to the present latex compositions in quantities that are well known to the art.

Also, in order to better achieve a homogeneous and stable latex composition, any insoluble additives that are added to the latex should be reduced in particle size to an optimum of about 5 micrometers and preferably added in dispersed or emulsified form in water.

- 15 Natural rubber latex is collected from the rubber-producing plants and trees, and a small quantity of a preservative is added to prevent premature coagulation before the latex is brought to a factory or processing center. Rubber collected in this manner is known as field latex.

- The main distinguishing feature of rubber products made from latex
20 rather than dry rubber is the rubber thickness, which is limited to a few millimeters. In producing latex products, the chemicals required for vulcanization, stiffening, coloring, antioxidant protection, or other purposes are added as solutions, emulsions, or fine dispersions to the latex before forming the product. Because no heat is generated during this mixing, it is possible to use ultrafast accelerators that would
25 cause scorch problems in dry rubber compounds.

The most important group of latex products are the dipped goods. As discussed above, these are produced by dipping a shaped former into a suitably formulated latex compound, and then withdrawing it. The latex deposit is dried and vulcanized in hot air to give the product, which is then stripped from the former.

Aside from dipping, the other main products produced from natural rubber latex are elastic thread and foam products.

Natural rubber latex also finds application in adhesives for tape, packaging, envelopes; in the footwear industry; and in the carpet industry.

5 The invention will be illustrated but not limited by the following examples.

EXAMPLES

Example 1

Preparation of the reaction product of decyl alcohol · 4EO and epichlorhydrin

10 About 150 grams of decyl alcohol ethoxylated with an average of 4 moles of ethylene oxide (0.45 OH equivalents) were mixed with 385 grams of toluene and 54 grams of 50% aq. NaOH (0.675 equivalents). The water was removed by azeotropic distillation and when a moisture level of less than 0.8% was reached, about 46 grams (0.51 equivalents) of epichlorhydrin were slowly added.
15 This mixture was allowed to react at 100° to 110°C for 24 hours. An aliquot of this mixture was removed and filtered to remove the NaCl and vacuum stripped to remove the toluene to give an amber, easily pourable liquid product that was dispersible in water.

Example 2

20 A natural rubber latex composition is prepared by mixing together the following components:

- A) a natural rubber latex which is a milky white liquid emulsion obtained from the cells of the Para rubber tree (*Hevea brasiliensis*); and
- B) 0.25% by weight of the reaction product of Example 1.

Example 3

Preparation of the reaction product of octyl alcohol · 4EO and epichlorohydrin

About 200.0 gm (0.654 hydroxyl equivs.) of octyl alcohol ethoxylated with an average of 4 moles of ethylene oxide was mixed with 400 gm toluene and 78.4 gm (0.98 equivs.) of 50% NaOH. Water was removed by azeotropic distillation until the level was below 0.8%. The mixture was cooled to 80°C. and 67.2 gm (0.72 moles) of epichlorohydrin was added over 45 mins. The mixture was stirred for 24 hrs at 110°C. until the epoxy titration showed no epoxide left. The material was cooled, filtered and the toluene was removed by vacuum distillation leaving a dark brown low viscosity liquid.

Example 4

A natural rubber latex composition is prepared from the following components:

- A) a natural rubber latex which is a milky white liquid emulsion obtained from the cells of the Para rubber tree (*Hevea brasiliensis*); and
- B) 1% by weight of the reaction product of Example 3.

Example 5

A ceramic mold for forming a latex glove is dipped into a tank containing the natural rubber latex composition of Example 2, to which is added a small quantity of sulfur and a dithiocarbamate. Excess latex is drained from the mold and the mold is dried at room temperature. The above process is repeated several times until the latex glove has the desired thickness. The latex glove is treated with hot air until the rubber is vulcanized, and is then removed from the mold. The latex glove is free from holes. The latex composition is stable and is substantially free from foam during the above procedure.

It will be appreciated by those skilled in the art that changes could be made to the embodiments described above without departing from the broad inventive concept thereof. It is understood, therefore, that this invention is not

limited to the particular embodiments disclosed, but it is intended to cover modifications within the spirit and scope of the present invention as defined by the appended claims.